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Carboranes

Substituent Effects on the Fluorescence Properties of *ortho*-Carboranes: Unusual Emission Behaviour in *C*-(2′-Pyridyl)-*ortho*-carboranes

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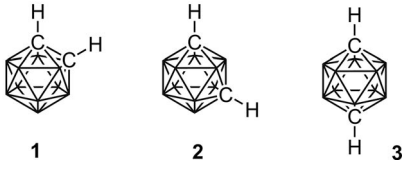
Dedicated to Professor Russell N. Grimes on the occasion of his 80th birthday

Abstract: Seventeen compounds including the parent *ortho*-, *meta*- and *para*-carboranes and derivatives of *ortho*-carborane were investigated for luminescence in cyclohexane and dichloromethane solutions. Fifteen of these carboranes revealed very weak emissions in the 285–493 nm range. These carboranes may arguably be viewed as non-emissive in solutions at room temperatures. No emissions could be observed for 1,2-dimethyl-*ortho*-carborane and 2-methyl-1-phenyl-*ortho*-carborane. The carboranes with a 2′-pyridyl substituent at the cluster carbon atom gave unusual local and charge-transfer emissions indicating that different excited states are generated on photoexcitation. Of all the carboranes investigated, only 2-(diphenylphosphino)-1-phenyl-*ortho*-carborane, 1,2-diphenyl-*ortho*-carborane and 1-phenyl-2-(2′-pyridyl)-*ortho*-carborane are luminescent in the solid state with emissions at 476–612 nm and large Stokes shifts of 12000–13600 cm^{-1}. The solid-state structures of 1,2-bis(2′-pyridyl)- and 1-phenyl-2-(2′-pyridyl)-*ortho*-carborane were determined by X-ray crystallography.

Introduction

Luminescence properties of derivatives of the dicarba-*closo*-dodecaborane isomers (1,2-, 1,7- and 1,12-$C_2B_{10}H_{12}$, which are *ortho*-, *meta*- and *para*-carborane **1**, **2** and **3**, respectively; Scheme 1),[1,2] have gained much interest recently.[3] Derivatives with *meta*- and *para*-carborane groups revealed luminescence properties characteristic of the non-carborane moieties.[4–13] The *meta*- or *para*-carborane cluster merely plays roles as a spectator, a spacer or an inductively electron-withdrawing group in these molecules or polymers. There are, however, rare exceptions where the clusters are actively involved in the excited states of bis(benzodiazaborolyl)-*meta*- and -*para*-carboranes.[9]



Scheme 1. Icosahedral carboranes **1**–**3**. Each naked vertex is BH.

The *ortho*-carboranyl group, on the other hand, can be a uniquely strong electron acceptor when connected to a donor at one or both cluster carbon atoms [at C1 and/or C2 in 1,2-$C_2B_{10}H_{12}$ (**1**)] due to the elasticity of the cluster C1–C2 bond.[14] The *ortho*-carborane unit can thus play an active role as the acceptor in organic donor–acceptor molecules (dyads). Photoexcitation of such dyads induced a charge transfer from an organic scaffold to the carborane cluster, which either led to luminescence quenching or to charge-transfer (CT) emissions or both – depending on the solvents used and whether the materials were investigated as solids.[7–13,15–28] Dual fluorescence with CT and local transitions has been observed in some *ortho*-carboranes.[12,13,15–20,28]

The *ortho*-carborane unit plays a role similar to *meta*- and *para*-carborane clusters in the photophysical process of a compound if there is a stronger electron acceptor than the cluster in these systems,[5,6,29,30] and if the *ortho*-carborane group is connected to a donor at one or more boron cluster atoms.[7,28,31] The *ortho*-carborane group is a much weaker electron acceptor when bonded at the boron atom (it may even be a donor depending on the position of the attached boron atom).[32]

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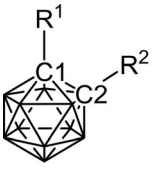
Recently, there have been considerable research efforts on the luminescence properties of iridium complexes with carborane clusters present.[33–37] Iridium complexes such as $Ir(ppy)_3$[38] have been studied in great depth for fifteen years due to their attractive phosphorescence properties as dopants in efficient light-emitting devices (LEDs).[39] While iridium complexes containing *meta*- and *para*-carboranes give subtle effects on the photophysics as expected,[34,35] those containing the *ortho*-carborane cluster yield very different luminescence properties provided that it is attached at the cluster carbon atom and is the electron acceptor in the photophysical processes. The luminescence of an iridium complex is therefore quenched or reduced significantly in this case.[35,36] If the *ortho*-carborane cluster is not the electron acceptor, it acts as an inductively electron-withdrawing group and can subtly influence the emission wavelength.[34,36,37]

Here we report our photophysical studies on the three parent carboranes **1**–**3** and fourteen *ortho*-carborane derivatives **4**–**17** with common substituents at the carborane carbon atoms (C1, C2) (Scheme 2). Only *ortho*-carboranes with substituents are explored here as varied photophysical properties have been noted earlier for *ortho*-carboranes. All carboranes – apart from **6** and **8** – are shown to fluoresce in cyclohexane and dichloromethane solutions at high concentrations. Thin films of **1**–**17** made by sublimation onto quartz plates revealed that only three, i.e. **15**–**17**, fluoresce in the solid state.

The carborane dithiol **9** is a well-known precursor to a vast field of metal complexes with carborane–thiolate ligands.[40] Some complexes made from **9** have been shown to luminesce with the carborane cluster acting as a spectator in these luminescence processes.[41] 1,2-Bis(phenylthio)-*ortho*-carborane, an analogue of **10** here, has been reported to luminesce at 406 nm.[42] The phosphine **12** is also a precursor to many metal complexes as a bidentate donor ligand, and the *closo*-carborane cage can, however, be converted into a *nido*-carborane anion during the reaction.[43] Phosphine **12** itself has been reported to be non-emissive,[44] and luminescent metal complexes containing **12** as ligand have so far been limited to a silver complex.[45]



	R^1	R^2
4	Me	H
5	$SiMe_3$	H
6	Me	Me
7	Ph	H
8	Ph	Me
9	SH	SH
10	SMe	SMe
11	PPh_2	H
12	PPh_2	PPh_2
13	2'-Py	H
14	2'-Py	2'-Py
15	Ph	PPh_2
16	Ph	Ph
17	Ph	2'-Py

Scheme 2. Substituted *ortho*-carboranes **4**–**17**, investigated in this study.

The pyridylcarborane **13** has been used as a precursor to luminescent iridium complexes analogous to the ubiquitous $Ir(ppy)_3$ dopant emitter.[33] Also other highly luminescent metal complexes have been reported with the pyridylcarborane unit present.[46] Given that there have been many articles on the observed luminescence of 1-monoalkyl-, 1-monoaryl- and 1,2-diaryl-*ortho*-carborane derivatives,[7–13,15–30] by contrast 1-monomethyl-*ortho*-carborane **4**, 1-monophenyl-*ortho*-carborane **7** and 1,2-diphenyl-*ortho*-carborane **16** were quoted to be non-emissive.[20,30]

Results and Discussion

Absorption

The absorption data for **1**–**17** in cyclohexane, dichloromethane and as sublimed thin films are listed in Table 1 and absorption

Table 1. Absorption data for **1**–**17**.

R^1	R^2		Cyclohexane Concentration[a]	Absorption maxima [nm] (extinction coefficient ε[L mol^{-1} cm^{-1}])	Dichloromethane Concentration[a]	Absorption maxima [nm] (extinction coefficient ε [L mol^{-1} cm^{-1}])	Film [nm][b]
H	H	**1**	53 mM	228 (2), 271 (<1)	43 mM	230 (1), 261 (<1), 282 (<1)	239
H	H	**2**	17 mM	251 (1), 282 (1)	18 mM	258 (1), 282 (1)	241
H	H	**3**	36 mM	283 (<1)	38 mM	235 (<1), 280 (<1)	241
Me	H	**4**	65 mM	273 (1)	56 mM	270 (1)	239
$SiMe_3$	H	**5**	27 mM	272 (1)	35 mM	271 (1)	238
Me	Me	**6**	42 mM	274 (<1)	43 mM	263 (<1)	241
Ph	H	**7**	100 μM	260 (380), 265 (410), 272 (310)	100 μM	260 (520), 265 (560), 272 (420)	267
Ph	Me	**8**	1.5 mM	260 (450), 266 (530), 272 (410)	2.3 mM	261 (440), 266 (510), 273 (390)	266
SH	SH	**9**	750 μM	*238*[c]	750 μM	*238*[c]	239
SMe	SMe	**10**	750 μM	*238*[c](*2960*)	750 μM	*238*[c] (*3900*)	239
PPh_2	H	**11**	200 μM	261 (5160), 268 (4960), 275 (3900)	200 μM	262 (3830), 267 (3670), 275 (2910)	274
PPh_2	PPh_2	**12**	50 μM	269 (10630), 275 (10870)	50 μM	269 (11600), 275 (11760)	238, 275
2′-Py	H	**13**	50 μM	257 (45760), 262 (52040), 269 (39290)	50 μM	257 (36850), 262 (41930), 268 (30040)	262
2′-Py	2′-Py	**14**	40 μM	261 (73850)	40 μM	262 (67850)	260
Ph	PPh_2	**15**	50 μM	262 (5280), 268 (5240), 277 (4250)	50 μM	262 (5190), 268 (5080), 276 (4220)	240, 278
Ph	Ph	**16**	100 μM	267 (1370), 274 (1200), 298 (480), 307 (260), 321 (210)	100 μM	267 (1570), 274 (1370), 298 (640), 309 (510), 323 (310)	238, 266
Ph	2′-Py	**17**	500 μM	257 (3560), 261 (3620)	500 μM	233 (8680), 257 (4890), 261 (5020)	259

[a] Concentration = molar concentration. [b] Film = sublimed thin film. [c] Estimated, no structured maximum.

spectra shown in Figures 1, 2, 3, and 4 and in Figures S1–S13. Carboranes **1**–**3** show very weak absorption bands in solutions as reported elsewhere (**1**: 252 nm with extinction coefficient ε = 0.4 L mol^{-1} cm^{-1} in *n*-hexane;[47] **2**: 239 nm with ε = 2.0 L mol^{-1} cm^{-1} in *n*-hexane;[47] **3**: 273 nm with ε = 3.2 L mol^{-1} cm^{-1} in dichloromethane[48]). Methyl and trimethylsilyl groups have little influence on the extinction coefficients or absorption maxima when the values for **4**–**6** are compared with **1**. Concentrations in the region of mM were necessary to record these weak bands (ε < 1 L mol^{-1} cm^{-1}) in **1**–**6**. Structured bands and higher coefficients (ε = 310–420 L mol^{-1} cm^{-1}) were observed in **7** and **8** where $\pi\rightarrow\pi^*$ transitions in the phenyl group present are responsible for these bands.[49,50] The absorption spectra for **9** or **10** showed one unstructured band slope tailing off at ca. 300 nm. Carboranes **11**–**17** contain bands with higher extinction coefficients (ε = 1200–73850 L mol^{-1} cm^{-1}) reflecting the presence of aryl groups with $\pi\rightarrow\pi^*$ transitions. The absorption spectra of sublimed thin films were broad and lacked fine structure with maxima observed in the range of 238–278 nm.

Emission and Excitation

Table 2 lists the emission and excitation data and Figures 1, 2, 3, and 4 and Figures S1–S13 depict emission and excitation spectra for **1**–**17** except for **6** and **8**. The excitation spectra shown here are the profile in the 2D emission-excitation spectra (EES) at the emission maximum (Figure S14). The *C*-methylcarboranes **6** and **8** did not show any emissions in solution. Most of the observed emissions were very weak with photoluminescence quantum yields (Φ^F) of less than 1 %. The Φ^F values listed in italics are those with large errors for such measurements as the very low absorption coefficients (ε < 1 L mol^{-1} cm^{-1}) combined with low fluorescence intensities result in significant uncertainties.

The parent carboranes **1**–**3** have not been reported to fluoresce in solutions at ambient temperatures prior to this study. Weak emissions from solutions of high concentrations were observed at 317–342 nm with Stokes shifts of 3970–7470 cm^{-1} (Figure 1 and Figure S1). The Stokes shift is calculated here as the difference between the low-energy excitation maximum and the high-energy emission maximum. The excitation maxima values are not necessarily the same as the absorption maxima values as the lowest-energy absorption maximum may not be observed. The latter band can be very weak or hidden in the low-energy tail end of a strong absorption band.

While most of the *ortho*-carborane derivatives follow the general photophysical pattern of **1**, there are some exceptions. The two derivatives with Ph_2P- or 2′-pyridyl groups at both carborane carbon atoms, **12** and **14**, contain structured emissions and small Stokes shifts of 210–1870 cm^{-1} and these emissions are based on local transitions at the aromatic rings. The carborane cluster in both compounds are not active in the radiative pathways here.

Table 2. Solution-state excitation (Ex), emission (Em) and quantum yield (QY) data for **1**–**5**, **7** and **9**–**17**.

R^1	R^2		Cyclohexane				Dichloromethane			
			Ex [nm]	Em [nm]	Stokes shift [cm^{-1}]	QY (Φ^F) [%]	Ex [nm]	Em [nm]	Stokes shift [cm^{-1}]	QY (Φ^F) [%]
H	H	**1**	275	317	4818	*1*	266	332	7474	*0.6*
H	H	**2**	280	315/329	3968	*4*	280	317/330/342	4169	*4*
H	H	**3**	280	325	4945	*1*	280	325	4945	*1*
Me	H	**4**	270	323	6077	*1*	270	324	6173	*0.7*
$SiMe_3$	H	**5**	268	286/311	2348	*1*	269	285/314	2087	*4*
Ph	H	**7**	278	328	5483	<0.5	284	334	5271	<0.5
SH	SH	**9**	295	353	5570	*<0.1*	275	358	8431	*<0.1*
SMe	SMe	**10**	332	410	5730	*<0.5*	332	410	5730	*<0.5*
PPh_2	H	**11**	313	339/353/436	2450	<0.1	311	359/435	4299	<0.1
PPh_2	PPh_2	**12**	414	428/442	790	3	416	451	1866	8
2′-Py	H	**13**	284	316	3566	<0.5	286	314	3118	<0.5
2′-Py	H	**13**	364	493	7189	0.8	338	418	5662	<0.5
2′-Py	2′-Py	**14**	308	310/322/332	209	<0.1	308	311/324/333	313	<0.1
Ph	PPh_2	**15**	298	346	4655	<0.1	298	346	4655	<0.1
Ph	Ph	**16**	292	348	5511	3	294	348	5278	4
Ph	2′-Py	**17**	286	329	4570	<0.1	366	442	4698	<0.1

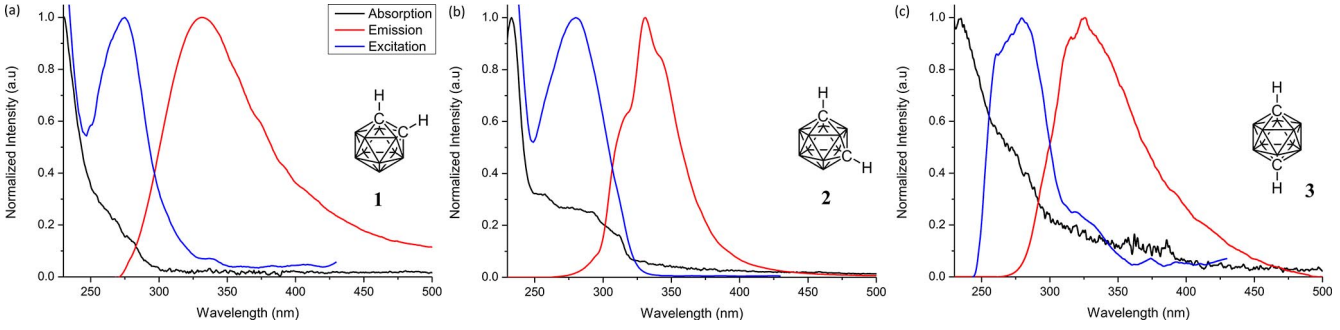


Figure 1. Absorption, emission and excitation spectra of (a) **1**, (b) **2** and (c) **3** in dichloromethane.

Two other exceptions to the general carborane spectra patterns are the 2-pyridylcarboranes **13** and **17**, where emissions are observed at different wavelengths. Compound **13** reveals two distinct emissions with the relative band intensities dependent on the excitation wavelengths (Figure 2 and Figure S14). It is possible that there are two distinct excited states. There is a strong intramolecular interaction between the pyridyl nitrogen atom and the carboranyl hydrogen atom in **13**, and these observed states relate to the presence or absence of hydrogen bonding.[51] Emission and excitation measurements on **13** were also carried out in other solvents (Table S1). Both emissions were observed with these solvents except for methanol and ethanol, where only the higher-energy emission could be seen. The low-energy emission for **13** does not have the solvatochromism character expected for a CT excited state as the emission wavelengths in some nonpolar solvents are longer than the emission wavelengths in some polar solvents. Negative solvatochromism may be implied, but there is no clear trend between the Stokes shift energies and the solvent polarities.

An *ortho*-carborane with a 2′-pyridyl–CH(OH)– substituent at C1 has been reported with different emission wavelengths at 349–384 nm in ethanol and 427–492 nm in the solid state.[52] It was implied that there are significant intermolecular interactions between molecules in the solid state not present in solution, thus different emission wavelengths are observed. For **13**, intramolecular interactions between the carboranyl protons and the pyridyl nitrogen atoms result in the low-energy emissions observed here.

The 1-phenyl-2-(2′-pyridyl)-*ortho*-carborane **17** is unique within the series here as the emission observed (Figure 3) is solvent-dependent with an emission maximum at 329 nm in cyclohexane and at 442 nm in dichloromethane. Based on reported photophysical data of other *ortho*-carboranes,[12,13,15–19] the emission at 329 nm is from local transitions at one or both aryl groups, whereas the emission at 442 nm is a charge transfer involving the carborane cluster. Low-energy emissions of **17** are also observed in toluene (440 nm), chloroform (408 nm) and acetonitrile (426 nm).

Solids of **1**–**17** were vacuum-sublimed onto quartz slides for photophysical measurements as carried out in our reported 1-borolyl- and 1-boryl-*ortho*-carborane investigations.[9,15,16,17] No thin-film emissions were observed at room temperatures for the parent carboranes **1**–**3**. Solid-state emissions at ambient temperatures were reported elsewhere for **1** (powder form: 395 nm;[53] silica gel form: 356 nm[5]), **2** (silica gel: 380 nm[5])

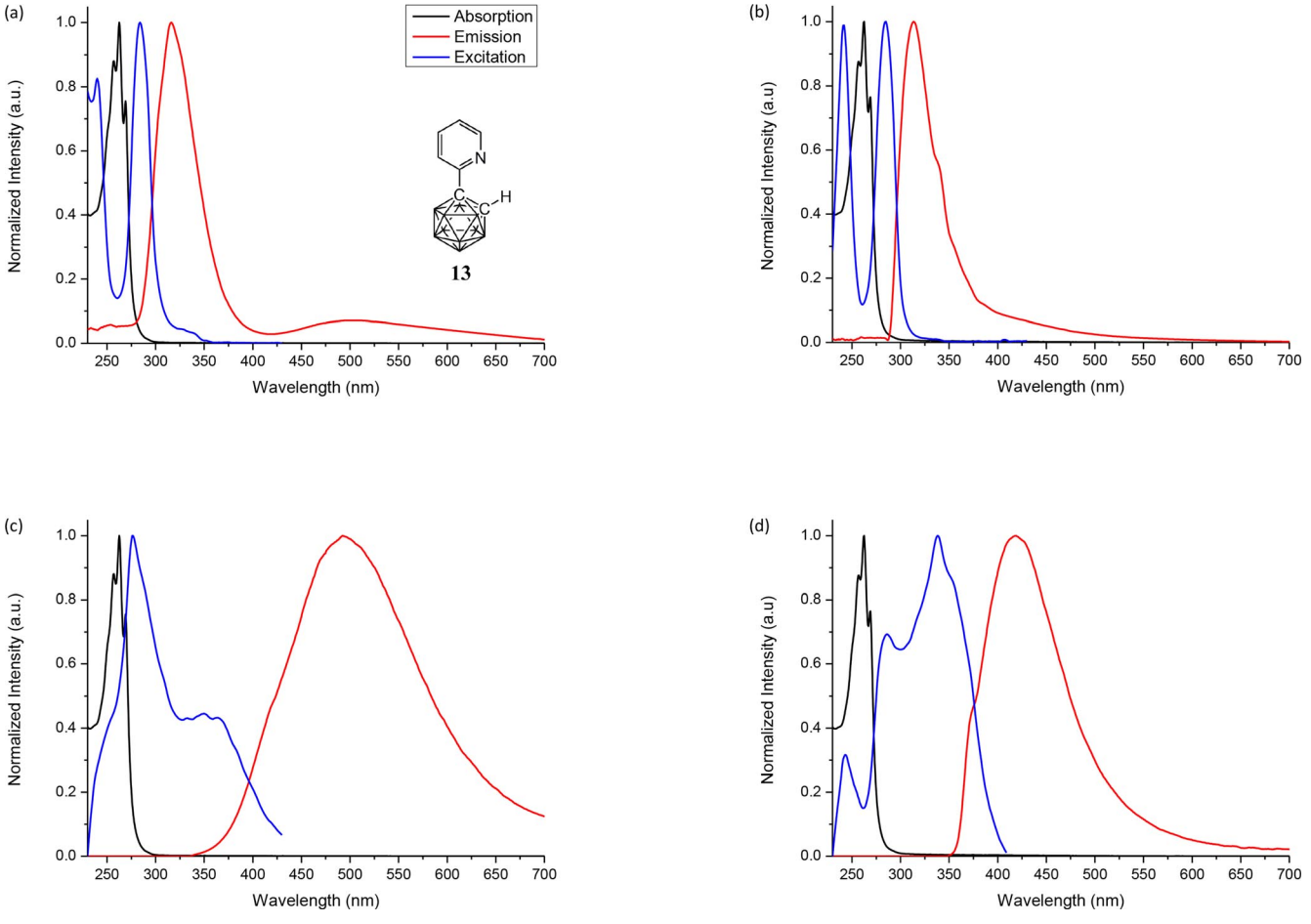


Figure 2. Absorption, emission and excitation spectra for **13** in (a) cyclohexane and (b) dichloromethane solutions with emission measured at 285 nm excitation wavelength and excitation determined at 316 and 314 nm emission wavelength and in (c) cyclohexane and (d) dichloromethane solutions with emission measured at 360 nm excitation wavelength and excitation determined at 493 and 418 nm emission wavelength.

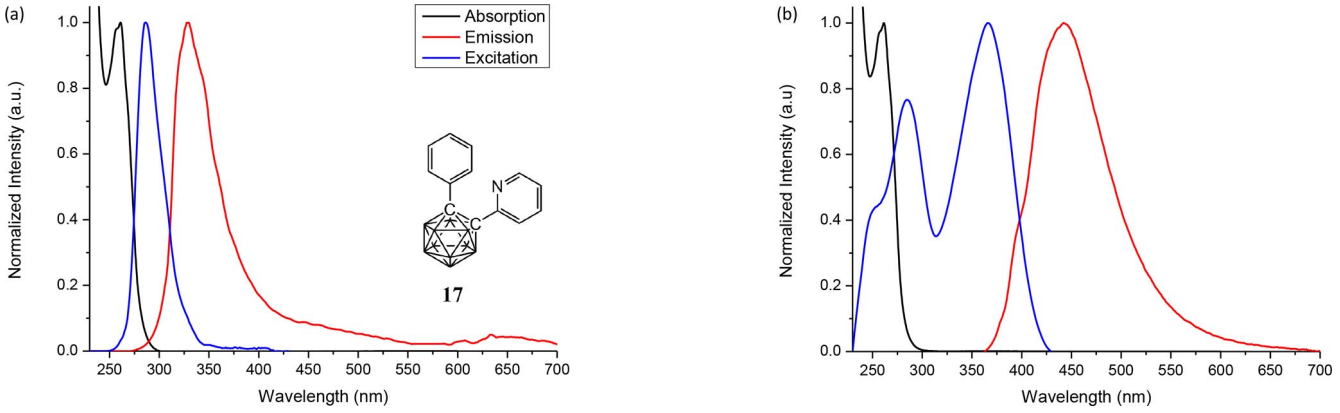


Figure 3. Absorption, emission and excitation spectra of **17** in (a) cyclohexane and (b) dichloromethane.

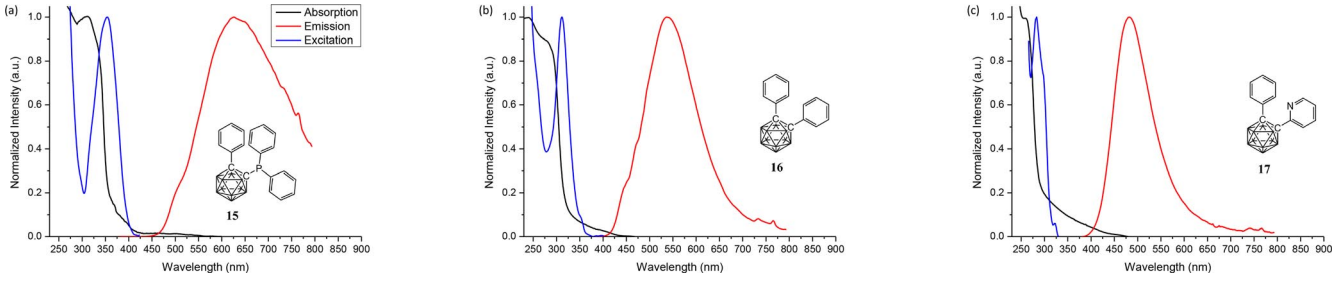


Figure 4. Absorption, emission and excitation spectra on sublimed thin films of (a) **15**, (b) **16** and (c) **17**.

and **3** (silica gel: 345 nm[5]). The different results are attributed to the different solid morphologies looked at. No emissions were observed from films of **4**–**14** either. However, low-energy emissions were observed for the aryl-*ortho*-carboranes **15**–**17** (Figure 4, Table 3) with quantum yields (Φ^F) of 2–9 % and large Stokes shifts of 12000–13600 cm^{-1}. The effect of the diphenylphosphino (Ph_2P), phenyl or 2′-pyridyl group at the second carbon atom of the 1-phenyl-*ortho*-carborane on the emission is reflected in the emission wavelengths: 612 nm for **15**, 537 nm for **16** and 476 nm for **17**. Such low-energy emissions have been reported in other diaryl-*ortho*-carboranes and arise from charge transfer involving both the ring and the carborane cluster.[9,10,13,15,16,18,20,22–26] The solid-state emission of 1,2-diphenyl-*ortho*-carborane **16** here is expected as many derivatives containing the diphenyl-*ortho*-carborane unit emit in the solid state.

Table 3. Thin film excitation (Ex), emission (Em) and quantum yield (QY) data for **15**–**17**.

R^1	R^2		Ex [nm]	Em [nm]	Stokes shift [cm^{-1}]	QY (Φ^F) [%]
Ph	PPh_2	**15**	353	612	11989	2
Ph	Ph	**16**	312	537	13429	7
Ph	2′-Py	**17**	289	476	13594	9

Crystallography

Crystal structures of **14** and **17** were obtained here (Figure 5) to give insight into why there are differences in the photophysical data in these compounds. The two independent molecules A and B in **14** revealed different pyridyl group orientations. The structures in both compounds have very similar C1–C2 bond lengths of 1.6838(17) (A) and 1.6918(17) Å (B) in **14** and 1.6955(16) Å in **17**. The aryl orientations between these molecules do vary with both rings perpendicular to the C1–C2 plane in **17** (maximising the overlap between the ring π orbital and the antibonding C1–C2 orbital) and may be responsible for the solid-state emission observed only for **17**. These findings do not explain the obvious differences in the photophysical data between the two carboranes in solution though. Table 4 lists all experimentally determined C1–C2 bond lengths for carboranes studied where available.[51,54–61] While disubstituted *ortho*-carboranes contain longer C1–C2 bonds than the monosubstituted

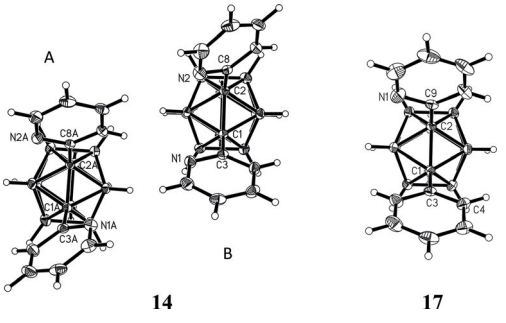


Figure 5. Molecular structures of **14** and **17** determined by X-ray crystallography. Two independent molecules A and B are present in the crystal of **14**. Selected torsion angles [°]: C1A–C2A–C8A–N2A –80.52(14), C2A–C1A–C3A–N1A –61.41(15), C1–C2–C8–N2 –61.28(15), C2–C1–C3–N1 90.19(14) for **14**; C1–C2–C9–N1 –88.4(13), C2–C1–C3–C4 93.10(14) for **17**. Thermal ellipsoids are at 50 % probability.

Table 4. Comparison of emission values with C1–C2 bond lengths and reduction potentials.

R^1	R^2		Emission maxima[a]			C1–C2 [Å][b]	*E*(Red) [V][c]	$E_{1/2}$ [V][d]
			CyH	DCM	Film			
H	H	**1**	317	332		1.620(3)[54]	*–3.09*	
H	H	**2**	315	317				
H	H	**3**	325	325				
Me	H	**4**	323	324		–	*–3.12*	
$SiMe_3$	H	**5**	286	285		–	*–3.01*	
Me	Me	**6**	–	–		–	*–3.00*	
Ph	H	**7**	328	334		1.649(2)[55]	*–2.48*	
Ph	Me	**8**	–	–		1.6954(16)[56]	*–2.24*	
SH	SH	**9**	353	358		–	*–1.43*	
SMe	SMe	**10**	410	410		1.803(2)[57]	*–1.76*	
PPh_2	H	**11**	339	359		1.666(9)[58]	*–2.54*	
PPh_2	PPh_2	**12**	428	451		1.7171(18)[59]	*–1.98*	
2′-Py	H	**13**	316	314		1.632(3)[51]	*–2.59*	
2′-Py	2′-Py	**14**	310	311		1.6838(17), 1.6918(17)	–1.75	–1.54
Ph	PPh_2	**15**	346	346	612	1.719(3), 1.737(3)[60]	*–1.75*	
Ph	Ph	**16**	348	348	537	1.722(2), 1.730(2)[61]	–1.80	–1.61
Ph	2′-Py	**17**	329	442	476	1.6955(16)	–1.74	–1.55

[a] Highest energy maximum listed in nm; CyH = cyclohexane, DCM = dichloromethane, film = sublimed thin film. [b] Most accurate carborane C1–C2 bond length from X-ray data where possible; the two reported values in some cases are from two independent molecules within the crystal. [c] Cathodic wave from cyclic-voltammetry measurements, values in italics are from irreversible waves. [d] First half-wave reduction potential of reversible waves.

ortho-carboranes, there is little correlation between these bond lengths and the emission data observed.

Cyclic Voltammetry

Cyclic voltammetry (CV) studies were carried out on carboranes **1**–**17** to obtain reduction potentials for comparison with observed emission data. No reduction waves were observed for the *meta*- and *para*-carboranes **2** and **3** within the acetonitrile solvent window. Only three compounds (**14**, **16** and **17**) showed reversible waves (Table S2); therefore, the cathodic wave values for **1** and **4**–**17** are listed in Table 4 for comparison. It has been shown elsewhere that CV studies of **1**,[62] **4**,[63] **6**,[63] **7**[63] and **12**[64] contain irreversible waves due to either carborane C–H or C–P cleavage, addition of a proton to the dianion formed, spontaneous deboronation of the dianion formed or combinations of these processes. For **4**, **11** and **13**, cleavage of the carborane C–H bond takes place on reduction. A decomposition process found[63] in the reduction of **6** occurs in the reduction of **8** as well. S–H bond cleavage follows on reduction of **9** based on the reported[65] electrochemical reduction of thiophenol. Cleavage of the carborane C–S bond occurs in **10** and likewise cleavage of the carborane C–P bond in **11** and **15** on the basis of a CV study[64] on related sulfur and phosphorus carboranes.

There is a general relationship between the reduction potentials and the C1–C2 bond lengths as indicated elsewhere.[16,66] Two groups are identified on this basis, one group with bond lengths of 1.62 (for **1**) to 1.67 Å (for **11**) gives reduction potentials of –3.09 (for **1**) to –2.54 V (for **11**), while another group containing longer bonds of 1.68 (for **14**) to 1.80 Å (for **10**) gives lower reduction potentials of –2.24 (for **8**) to –1.74 V (for **17**). However, there is little correlation between the emission data and the CV data, which is perhaps expected as reduction potentials only give an estimate for the relative LUMO energies. The energy differences between the HOMOs and LUMOs can be predicted if oxidation waves in these carboranes were observed and the energy differences would have a better correlation with the emission maxima observed.

Of the three carboranes with poorly resolved two-electron reversible waves observed, dipyridyl-*ortho*-carborane **14** and 1-phenyl-2-(2′-pyridyl)-*ortho*-carborane **17** are easier to reduce than diphenyl-*ortho*-carborane **16**,[5,61–63,67] and 1-phenyl-2-(2′-pyridyl)-*ortho*-carborane **17**. This observation suggests that the carborane moiety is a suitable acceptor in **14** and thus gives charge-transfer emissions. These CT emissions are quenched for **14** in solutions and in the solid state, even though very weak absorption bands are found in the 350 nm region in solutions for **14** (Figure S15).

Conclusions

Our photophysical measurements on the parent carboranes **1**–**3** and fourteen derivatives **4**–**17** of *ortho*-carborane reveal that all – except two (1,2-dimethyl- and 2-methyl-1-phenyl-*ortho*-carboranes **6** and **8**, respectively) – are emissive in concentrated solutions (cyclohexane and dichloromethane). However, the vast majority of these compounds give very weak emissions; thus, these carboranes are considered (and have been reported for **4**,[30] **7**,[30] **12**[44] and **16**[20]) as non-emissive. The influence of the substituents, Me, SH, SMe and $SiMe_3$, on the photophysics of *ortho*-carborane is subtle, whereas the influence of the aryl groups, Ph, PPh_2 and 2′-pyridyl, is inevitably present with π–π^* transitions and/or charge-transfer emissions.

The effect of the 2′-pyridyl group on the photophysics of *ortho*-carborane is remarkable. The monopyridylcarborane **13** revealed low- and high-energy emissions – arising from two excited states formed from two initial ground states with one involving an intramolecular hydrogen bond. The 1,2-dipyridyl-carborane **14** gave a high-energy emission consistent with local ring transitions, while emission of 1-phenyl-2-(2′-pyridyl)-*ortho*-carborane **17** is solvent-dependent affording a high-energy

emission (329 nm) in cyclohexane and a low-energy emission (442 nm) in dichloromethane.

Examination of the photophysics on thin films of compounds **1**–**17** made by sublimation showed that only three were detected to be fluorescent with emission maxima at 612 nm [2-(diphenylphosphino)-1-phenyl-*ortho*-carborane, **15**], 537 nm (1,2-diphenyl-*ortho*-carborane, **16**) and 476 nm [1-phenyl-2-(2′-pyridyl)-*ortho*-carborane, **17**]. While the observed solid-state emission of **16** is expected as many derivatives containing the diphenyl-*ortho*-carborane unit are luminescent in the solid state, the use of a Ph_2P- or 2′-pyridyl group in place of one phenyl group is intriguing. Derivatives containing a 2-(diphenylphosphino)-1-phenyl- or a 1-phenyl-2-(2′-pyridyl)carborane unit may also be notably emissive in the solid state and at longer and shorter wavelengths, respectively, compared to the emission wavelength from the diphenylcarborane unit.

Any correlations between the emission maxima of the *ortho*-carboranes studied here with their reduction potentials and their experimental carborane C1–C2 bond lengths were not found. For example, the crystal structures and reduction potentials of **14** and **17** determined here were very similar, yet their emission data were remarkably different. Nevertheless, the photophysical data reported here provide a useful databank for photophysical studies on new carborane-containing derivatives with intriguing luminescence properties carried out here and elsewhere.

Experimental Section

Syntheses: Compounds **1**–**3** were purchased commercially (KatChem) and purified by repeated sublimations, whereas **4**,[68] **5**,[69] **6**,[68] **7**,[69] **8**,[70] **9**,[71] **10**,[71] **11**,[72] **12**,[73] **13**,[74] **14**,[74] **15**,[72] **16**[75] and **17**[74] were prepared according to literature procedures. ^{13}C NMR spectroscopic data in $CDCl_3$ calibrated on the solvent signal at δ = 77.0 ppm; **5**: δ = 66.2 (C1), 59.7 (C2 H), –1.5 (CH_3) ppm; **15**: δ = 135.4 (d, $^2J_{PC}$ = 27 Hz, *ortho*-PPh_2), 132.8 (d, $^1J_{PC}$ = 15 Hz, *ipso*-PPh_2), 131.9 (d, $^4J_{PC}$ = 2, *para*-PPh_2), 131.2 (d, $^3J_{PC}$ = 4 Hz, *ipso*-phenyl C), 130.9 (s, *ortho*-phenyl C), 130.6 (s, *para*-phenyl C), 128.5 (d, $^3J_{PC}$ = 10 Hz, *meta*-PPh_2), 86.0 (d, $^2J_{PC}$ = 20 Hz, C1), 83.2 (d, $^1J_{PC}$ = 72 Hz, C2) ppm; **17**: δ = 148.9 (C6′), 148.7 (C2′), 136.6 (C4′), 130.7 (*ortho*- and *ipso*-phenyl C), 130.0 (*para*-phenyl C), 128.0 (*meta*-phenyl C), 124.9 (C3′), 124.3 (C5′), 84.7 (C1), 84.1 (C2) ppm.

Photophysical Measurements: Absorption spectra were measured from 200 to 600 nm ($\Delta\lambda$ = 0.5 nm) with a Shimadzu absorption spectrometer. In most cases, the sample concentrations (Table 1) used for the absorption measurements were too low to obtain the excitation-emission spectra. Samples with significantly higher concentrations were therefore used to obtain the excitation-emission spectra. For every substance measurement, a spectrum of the pure solvent was measured to ensure that the cuvette and the solvent were free of any luminescent impurities. The sample was then dissolved directly in the solvent within the cuvette. The samples were generally excited from 230 nm to 430 nm ($\Delta\lambda$ = 0.5 nm). The excitation monochromator entrance and exit slits were opened at 3 mm during the measurements. For weak emissions, longer integration times were used for the samples at 230 to 330 nm excitation without lengthening the time of measurement. The emission wavelengths were separated by a grating with 150 lines/mm using a central wavelength of 500 nm. The entrance slits of the emission monochromator were opened at 25 μm. The spectra were measured with 10 s integration time/nm in most cases. Substances with stronger emissions were measured with 4 s integration time.

For the solid-state photophysical measurements, each substance in a flask was sublimed onto quartz plates (35 × 10 × 1 mm) with an operating vacuum pressure of 10^{-2} to 10^{-3} mbar using a Schlenk vacuum line. The substance at the bottom of the flask was heated to the initial sublimation temperature of the particular carborane (40–150 °C region) until a thin film was observed on the plate. Optical densities were not determined as the film thicknesses were variable; thus, normalized data are reported here. While the solid morphologies of the films differ as expected from the crystals of the carborane samples, the observed fluorescence of the carborane crystals and films are identical to the naked eye under a UV lamp (365 nm). The thin-film spectra were detected with an edge filter (360 nm) in front of the emission monochromator to block the excitation light.

Stokes shifts were calculated from the difference between excitation and emission spectra in wavenumbers. When more maxima are observed in excitation and/or emission the most redshifted excitation maximum and the most blueshifted emission maximum are used. The quantum yields in solution were determined against the standard POPOP [1,4-bis(5-phenyloxazol-2-yl)benzene, Φ = 0.93], while quantum yields of the thin films were determined with the integration-sphere setup according to the Mello method.[76] The emission of a thin film was measured in the integration sphere with excitation at 290 nm. The sample was placed in the centre of the sphere where direct excitation takes place for the first measurement (index: X_in). The sample was in a position where only indirect excitation with scattered light takes place for the second measurement (index: X_out). A quartz plate without the sample was also measured (X_LM) as background. The difference in the integrated scattering signal (X) of both sample and background plates gives the absorption (*A*), while the emission is determined from the integration of the fluorescence signal (*E*) with the equations as

$$A = (X\_out - X\_in)/X\_out$$

and

$$QY = [E\_in - (1 - A)\cdot E\_out]/(X\_LM\cdot A)$$

Crystallography: The single-crystal X-ray data were collected at 120 K with the Bruker D8Venture diffractometer [Photon100 CMOS detector, IμS-microsource, focusing mirrors, λ(Mo-K_α), λ = 0.71073 Å, ω-scan, 1°/frame] equipped with Cryostream (Oxford Cryosystems) open-flow nitrogen cryostates. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 for all data using SHELXTL[77] and OLEX2[78] software. All non-hydrogen atoms were refined with anisotropic displacement parameters, H atoms were located on the difference map and refined isotropically. In molecule B, the Py ring shows a 0.8:0.2 disorder by 180° rotation around the C2–C8 bond with the major component shown in Figure 5. Crystal data and experimental details are given in Table S3. CCDC 1435093 (for **14**), and 1435094 (for **17**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Cyclic Voltammetry: Cyclic-voltammetry measurements were carried out with an EcoChemie Autolab PG-STAT 30 potentiostat at 298 K with a glassy carbon working electrode and platinum wires as counter and reference electrodes in a nitrogen-containing glove box with 0.1 M nBu_4NPF_6 in acetonitrile. Scan rates of 100 mV s^{-1} were used. The ferrocene/ferrocenium FcH/FcH^+ couple served as internal reference at 0.0 V for potential measurements, and peak-

peak separations of this couple were generally in the region of 90–110 mV.

Supporting Information (see footnote on the first page of this article): Figures of solution-state absorption spectra for **1**–**12** and **14**–**16**, emission and excitation spectra for **1**–**5**, **7**, **9**–**12** and **14**–**16**, 2D emission-excitation spectra (EES) for **13** in chloroform, solution-state absorption spectra of **13**, **14** and **17** at high concentrations and CV traces for **1** and **4**–**17**; tables of emission data for **13** in various solvents, CV data for **14**, **16** and **17** and crystallographic data for **14** and **17**.

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[1] R. N. Grimes, *Carboranes*,, 2nd ed., Academic Press (Elsevier), New York, **2011**.

[2] For other reviews on carboranes see: a) V. I. Bregadze, *Chem. Rev.* **1992**, *92*, 209–223; b) L. A. Leites, *Chem. Rev.* **1992**, *92*, 279–323; c) J. F. Valliant, K. J. Guenther, A. S. King, P. Morel, P. Schaffer, O. O. Sogbein, K. A. Stephenson, *Coord. Chem. Rev.* **2002**, *232*, 173–230; d) T. J. Wedge, M. F. Hawthorne, *Coord. Chem. Rev.* **2003**, *240*, 111–128; e) M. A. Fox, A. K. Hughes, *Coord. Chem. Rev.* **2004**, *248*, 457–476; f) A. F. Armstrong, J. F. Valliant, *Dalton Trans.* **2007**, 4240–4251; g) M. A. Fox, "Polyhedral Carboranes" in *Comprehensive Organometallic Chemistry III* (Eds.: R. H. Crabtree, D. M. P. Mingos), Elsevier, Oxford, **2007**, vol. 3, chapter 3.02, pp. 49–112; h) V. N. Kalinin, V. A. Ol'shevskaya, *Russ. Chem. Bull. Int. Ed.* **2008**, *57*, 815–836; i) I. B. Sivaev, V. V. Bregadze, *Eur. J. Inorg. Chem.* **2009**, 1433–1450; j) F. Issa, M. Kassiou, L. M. Rendina, *Chem. Rev.* **2011**, *111*, 5701–5722; k) M. Scholz, E. Hey-Hawkins, *Chem. Rev.* **2011**, *111*, 7035–7062; l) Z. J. Leśnikowski, "New opportunities in boron chemistry for medical applications" in *Boron Science* (Ed.: N. S. Hosmane), CRC Press, New York, **2012**, chapter 1, p. 3–19; m) S. Stadlbauer, E. Hey-Hawkins, "Bioconjugates of carbaboranyl phosphonates", in *Boron Science* (Ed.: N. S. Hosmane), CRC Press, New York, **2012**, chapter 2, pp. 21–39; n) H. K. Agarwal, S. Hasabelnaby, R. Tiwari, W. Tjarks, "Boron cluster (radio)halogenation in biomedical research" in *Boron Science* (Ed.: N. S. Hosmane), CRC Press, New York, **2012**, chapter 6, pp. 107–144; o) H. Nakamura, "Polyhedral boron compounds for BNCT" in *Boron Science* (Ed.: N. S. Hosmane), CRC Press, New York, **2012**, chapter 8, pp. 165–179; p) V. I. Bregadze, I. B. Sivaev, "Polyhedral boron compounds for BNCT" in *Boron Science* (Ed.: N. S. Hosmane), CRC Press, New York, **2012**, chapter 9, pp. 181–209; q) M. Sibrian-Vazquez, M. G. H. Vicente, "Boron tumor delivery for BNCT" in *Boron Science* (Ed.: N. S. Hosmane), CRC Press, New York, **2012**, chapter 10, pp. 209–241; r) B. P. Dash, R. Satapathy, J. A. Maguire, N. S. Hosmane, "Carborane clusters" in *Boron Science* (Ed.: N. S. Hosmane), CRC Press, New York, **2012**, chapter 26, pp. 675–699; s) C. Viñas, R. Núñez, F. Teixidor, "Large molecules containing icosahedral boron clusters designed for potential applications" in *Boron Science* (Ed.: N. S. Hosmane), CRC Press, New York, **2012**, chapter 27, pp. 701–740; t) D. Olid, C. Viñas, F. Teixidor, *Chem. Soc. Rev.* **2013**, *42*, 3318–3336; u) V. I. Bregadze, *Russ. Chem. Bull. Int. Ed.* **2014**, *63*, 1021–1026.

[3] a) A. Nagai, Y. Chujo, *Chem. Lett.* **2010**, *39*, 430–435; b) B. P. Dash, R. Satapathy, J. A. Maguire, N. S. Hosmane, *New J. Chem.* **2011**, *35*, 1955–1972; c) P. A. Jelliss, "Photoluminescence from boron-based polyhedral clusters" in *Boron Science* (Ed.: N. S. Hosmane), CRC Press, New York, **2012**, chapter 15, pp. 355–382; d) R. N. Grimes, *Dalton Trans.* **2015**, *44*, 5939–5956.

[4] a) M. Ghirotti, P. F. H. Schwab, M. T. Indelli, C. Chiorboli, F. Scandola, *Inorg. Chem.* **2006**, *45*, 4331–4333; b) J.-F. Morin, T. Sasaki, Y. Shirai, J. M. Guerrero, J. M. Tour, *J. Org. Chem.* **2007**, *72*, 9481–9490; c) A. M. Prokhorov, P. A. Slepukhin, V. L. Rusinov, V. N. Kalinin, D. N. Kozhevnikov, *Tetrahedron Lett.* **2008**, *49*, 3785–3789; d) J. J. Peterson, Y. C. Simon, E. B. Coughlin, K. R. Carter, *Chem. Commun.* **2009**, 4950–4952; e) K. Kokado, Y. Tokoro, Y. Chujo, *Macromolecules* **2009**, *42*, 2925–2930; f) S. Khatua, J. M. Guerrero, K. Claytor, G. Vives, A. B. Kolomeishy, J. M. Tour, S. Link, *ACS Nano* **2009**, *3*, 351–356; g) S. Khatua, J. Godoy, J. M. Tour, S. Link, *J. Phys. Chem. Lett.* **2010**, *1*, 3288–3291; h) G. Vives, J. M. Guerrero, J. Godoy, S. Khatua, Y.-P. Wang, J. L. Kiappes, S. Link, J. M. Tour, *J. Org. Chem.* **2010**, *75*, 6631–6643; i) J. Godoy, G. Vives, J. M. Tour, *Org. Lett.* **2010**, *12*, 1464–1467; j) R. Ziessel, G. Ulrich, J. H. Olivier, T. Bura, A. Sutter, *Chem. Commun.* **2010**, *46*, 7978–7980; k) J.-F. Nicoud, F. Bolze, X.-H. Sun, A. Hayek, P. Baldeck, *Inorg. Chem.* **2011**, *50*, 4272–4278; l) D. Hablot, A. Sutter, P. Retailleau, R. Ziessel, *Chem. Eur. J.* **2012**, *18*, 1890–1895; m) D. Hablot, R. Ziessel, M. A. H. Alamiry, E. Bahraidah, A. Harriman, *Chem. Sci.* **2013**, *4*, 444–453; n) A. Harriman, M. A. H. Alamiry, J. P. Hagon, D. Hablot, R. Ziessel, *Angew. Chem. Int. Ed.* **2013**, *52*, 6611–6615; *Angew. Chem.* **2013**, *125*, 6743–6747; o) M. T. Indelli, T. Bura, R. Ziessel, *Inorg. Chem.* **2013**, *52*, 2918–2926.

[5] J. H. Gibbs, H. Wang, N. V. S. D. K. Bhupathiraju, F. R. Fronczek, K. M. Smith, M. G. H. Vicente, *J. Organomet. Chem.* **2015**, *798*, 209–213.

[6] O. Crespo, M. C. Gimeno, A. Laguna, I. Ospina, G. Aullon, J. M. Oliva, *Dalton Trans.* **2009**, 3807–3813.

[7] L. Zhu, W. Lv, S. Liu, H. Yan, Q. Zhao, W. Huang, *Chem. Commun.* **2013**, *49*, 10638–10640.

[8] K. Kokado, Y. Tokoro, Y. Chujo, *Macromolecules* **2009**, *42*, 9238–9242.

[9] L. Weber, J. Kahlert, R. Brockhinke, L. Böhling, J. Halama, A. Brockhinke, H.-G. Stammler, B. Neumann, C. Nervi, R. A. Harder, M. A. Fox, *Dalton Trans.* **2013**, *42*, 10982–10996.

[10] K.-R. Wee, Y.-J. Cho, S. Jeong, S. Kwon, J.-D. Lee, I.-H. Suh, S. O. Kang, *J. Am. Chem. Soc.* **2012**, *134*, 17982–17990.

[11] B. P. Dash, R. Satapathy, E. R. Galliard, K. M. Norton, J. A. Maguire, N. Chug, N. S. Hosmane, *Inorg. Chem.* **2011**, *50*, 5485–5493.

[12] S. Kwon, K.-R. Wee, Y.-J. Cho, S. O. Kang, *Chem. Eur. J.* **2014**, *20*, 5953–5960.

[13] K.-R. Wee, W.-S. Han, D. W. Cho, S. Kwon, C. Pac, S. O. Kang, *Angew. Chem. Int. Ed.* **2012**, *51*, 2677–2680; *Angew. Chem.* **2012**, *124*, 2731–2734.

[14] a) D. A. Brown, W. Clegg, H. M. Colquhoun, J. A. Daniels, I. R. Stephenson, K. Wade, *J. Chem. Soc., Chem. Commun.* **1987**, 889–891; b) T. D. Getman, C. B. Knobler, M. F. Hawthorne, *J. Am. Chem. Soc.* **1990**, *112*, 4593–4594; c) T. D. Getman, C. B. Knobler, M. F. Hawthorne, *Inorg. Chem.* **1992**, *31*, 101–105; d) J. Llop, C. Viñas, J. M. Oliva, F. Teixidor, M. A. Flores, R. Kivekäs, R. Sillanpää, *J. Organomet. Chem.* **2002**, *657*, 232–238; e) L. A. Boyd, W. Clegg, R. C. B. Copley, M. G. Davidson, M. A. Fox, T. G. Hibbert, J. A. K. Howard, A. Mackinnon, R. J. Peace, K. Wade, *Dalton Trans.* **2004**, 2786–2799; f) J. M. Oliva, N. L. Allan, P. v. R. Schleyer, C. Viñas, F. Teixidor, *J. Am. Chem. Soc.* **2005**, *127*, 13538–13547.

[15] L. Weber, J. Kahlert, R. Brockhinke, L. Böhling, A. Brockhinke, H.-G. Stammler, B. Neumann, R. A. Harder, M. A. Fox, *Chem. Eur. J.* **2012**, *18*, 8347–8357.

[16] L. Weber, J. Kahlert, L. Böhling, A. Brockhinke, H.-G. Stammler, B. Neumann, R. A. Harder, P. J. Low, M. A. Fox, *Dalton Trans.* **2013**, *42*, 2266–2281.

[17] J. Kahlert, L. Böhling, A. Brockhinke, H.-G. Stammler, B. Neumann, L. M. Rendina, P. J. Low, L. Weber, M. A. Fox, *Dalton Trans.* **2015**, *44*, 9766–9781.

[18] S.-Y. Kim, Y.-J. Cho, G. F. Jin, W.-S. Han, H.-J. Son, D. W. Cho, S. O. Kang, *Phys. Chem. Chem. Phys.* **2015**, *17*, 15679–15682.

[19] S.-Y. Kim, A.-R. Lee, Y.-J. Cho, H.-J. Son, W.-S. Han, S. O. Kang, *J. Organomet. Chem.* **2015**, *798*, 245–251.

[20] K.-R. Wee, Y.-J. Cho, J. K. Song, S. O. Kang, *Angew. Chem. Int. Ed.* **2013**, *52*, 9682–9685; *Angew. Chem.* **2013**, *125*, 9864–9867.

[21] S.-Y. Kim, A.-R. Lee, G. F. Jin, Y.-J. Cho, H.-J. Son, W.-S. Han, S. O. Kang, *J. Org. Chem.* **2015**, *80*, 4573–4580.

[22] H. J. Bae, H. Kim, K. M. Lee, T. Kim, Y. S. Lee, Y. Do, M. H. Lee, *Dalton Trans.* **2014**, *43*, 4978–4985.

[23] a) J. J. Peterson, M. Werre, Y. C. Simon, E. B. Coughlin, K. R. Carter, *Macromolecules* **2009**, *42*, 8594–8598; b) J. J. Peterson, A. R. Davis, M. Werre, E. B. Coughlin, K. R. Carter, *ACS Appl. Mater. Interfaces* **2011**, *3*, 1796–1799; c) A. R. Davis, J. J. Peterson, K. R. Carter, *ACS Macro Lett.* **2012**, *1*, 469–472.

[24] S. Inagi, K. Hosoi, T. Kubo, N. Shida, T. Fuchigami, *Electrochemistry* **2013**, *81*, 368–370.

[25] a) K. Kokado, Y. Chujo, *Macromolecules* **2009**, *42*, 1418–1420; b) K. Kokado, A. Nagai, Y. Chujo, *Macromolecules* **2010**, *43*, 6463–6468; c) K. Kokado, Y. Chujo, *Polym. J.* **2010**, *42*, 363–367; d) K. Kokado, Y. Chujo, *Dalton Trans.* **2011**, *40*, 1919–1923; e) K. Kokado, Y. Chujo, *J. Org. Chem.* **2011**, *76*, 316–319.

[26] K. Kokado, A. Nagai, Y. Chujo, *Tetrahedron Lett.* **2011**, *52*, 293–296.

[27] a) A. Ferrer-Ugalde, E. J. Juárez-Pérez, F. Teixidor, C. Viñas, R. Sillanpää, E. Pérez-Inestrosa, R. Núñez, *Chem. Eur. J.* **2012**, *18*, 544–553; b) M. Eo, M. H. Park, T. Kim, Y. Do, M. H. Lee, *Polymer* **2013**, *54*, 6321–6328; c) A. Ferrer-Ugalde, A. González-Campo, C. Viñas, J. Rodriguez-Romero, R. Santillan, N. Farfán, R. Sillanpää, A. Sousa-Pedrares, R. Núñez, F. Teixidor, *Chem. Eur. J.* **2014**, *20*, 9940–9951.

[28] a) M. Tominaga, H. Naito, Y. Morisaki, Y. Chujo, *Asian J. Org. Chem.* **2014**, *3*, 624–631; b) M. Tominaga, H. Naito, Y. Morisaki, Y. Chujo, *New J. Chem.* **2014**, *38*, 5686–5690.

[29] a) E. Hong, H. Jang, Y. Kim, S. C. Jeoung, Y. Do, *Adv. Mater.* **2001**, *13*, 1094–1096; b) C. H. Shin, Y. Han, M. H. Lee, Y. Do, *J. Organomet. Chem.* **2009**, *694*, 1623–1631; c) R. Luguya, F. R. Fronczek, K. M. Smith, M. G. H. Vicente, *Appl. Radiat. Isot.* **2004**, *61*, 1117–1123; d) V. N. Luzgina, V. A. Ol'shevskaya, A. V. Sekridova, A. F. Mironov, V. N. Kalinin, V. Z. Pashchenko, V. V. Gorokhov, V. B. Tusov, A. A. Shtil', *Russ. J. Org. Chem.* **2007**, *43*, 1243–1251; e) Y. C. Simon, J. J. Peterson, C. Mangold, K. R. Carter, E. B. Coughlin, *Macromolecules* **2009**, *42*, 512–516; f) B. P. Dash, R. Satapathy, J. A. Maguire, N. S. Hosmane, *Chem. Commun.* **2009**, 3267–3269; g) B. P. Dash, R. Satapathy, E. R. Gaillard, J. A. Maguire, N. S. Hosmane, *J. Am. Chem. Soc.* **2010**, *132*, 6578–6587; h) K. Kokado, M. Tominaga, Y. Chujo, *Macromol. Rapid Commun.* **2010**, *31*, 1389–1394; i) G. Pieters, A. Gaucher, D. Prim, T. Besson, J. G. Planas, F. Teixidor, C. Vinas, M. E. Light, M. B. Hursthouse, *Chem. Commun.* **2011**, *47*, 7725–7727; j) M. H. Park, K. M. Lee, T. Kim, Y. Do, M. H. Lee, *Chem. Asian J.* **2011**, *6*, 1362–1366; k) F. Lerouge, A. Ferrer-Ugalde, C. Viñas, F. Teixidor, R. Sillanpää, A. Abreu, E. Xochitiotzi, J. Rodriguez-Romero, N. Farfán, R. Santillan, R. Núñez, *Dalton Trans.* **2011**, *40*, 7541–7550; l) Y. Morisaki, M. Tominaga, Y. Chujo, *Chem. Eur. J.* **2012**, *18*, 11251–11257; m) K. C. Song, H. Kim, K. M. Lee, Y. S. Lee, Y. Do, M. H. Lee, *Dalton Trans.* **2013**, *42*, 2351–2354; n) G. Y. Atmaca, C. Dizman, T. Eren, A. Erdğmuş, *Spectrochim. Acta Part A* **2015**, *137*, 244–249; o) H. Naito, Y. Morisaki, Y. Chujo, *Angew. Chem. Int. Ed.* **2015**, *54*, 5084–5087; *Angew. Chem.* **2015**, *127*, 5173–5176; p) G. F. Jin, Y.-J. Cho, K.-R. Wee, S. A. Hong, I.-H. Suh, H.-J. Son, J.-D. Lee, W.-S. Han, D. W. Cho, S. O. Kang, *Dalton Trans.* **2015**, *44*, 2780–2787; q) M. Tominaga, K. Nishino, Y. Morisaki, Y. Chujo, *J. Organomet. Chem.* **2015**, *798*, 165–170.

[30] F. Lerouge, C. Viñas, F. Teixidor, R. Núñez, A. Abreu, E. Xochitiotzi, R. Santillan, N. Farfán, *Dalton Trans.* **2007**, 1898–1903.

[31] V. Z. Paschenko, R. P. Evstigneeva, V. V. Gorokhov, V. N. Luzgina, V. B. Tusov, A. B. Rubin, *J. Photochem. Photobiol. B* **2000**, *54*, 162–167.

[32] V. N. Kalinin, N. I. Kobel'kova, A. V. Astakhin, A. I. Gusev, L. I. Zakharkin, *J. Organomet. Chem.* **1978**, *149*, 9–21.

[33] H. J. Bae, H. Kim, K. M. Lee, T. Kim, M. Eo, Y. S. Lee, Y. Do, M. H. Lee, *Dalton Trans.* **2013**, *42*, 8549–8552.

[34] a) C. Shi, D. Tu, Q. Yu, H. Liang, Y. Liu, Z. Li, H. Yan, Q. Zhao, W. Huang, *Chem. Eur. J.* **2014**, *20*, 16550–16557; b) L. Zhu, X. Tang, Q. Yu, W. Lv, H. Yan, Q. Zhao, W. Huang, *Chem. Eur. J.* **2015**, *21*, 4721–4730.

[35] a) C. Shi, H. Sun, X. Tang, W. Lv, H. Yan, Q. Zhao, J. Wang, W. Huang, *Angew. Chem. Int. Ed.* **2013**, *52*, 13434–13438; *Angew. Chem.* **2013**, *125*, 13676–13680; b) C. Shi, H. Sun, Q. Jiang, Q. Zhao, J. Wang, W. Huang, H. Yan, *Chem. Commun.* **2013**, *49*, 4746–4748.

[36] a) T. Kim, H. Kim, K. M. Lee, Y. S. Lee, M. H. Lee, *Inorg. Chem.* **2013**, *52*, 160–168; b) Y. H. Lee, J. Park, S.-J. Jo, M. Kim, J. Lee, S. U. Lee, M. H. Lee, *Chem. Eur. J.* **2015**, *21*, 2052–2061; c) Y. H. Lee, J. Park, J. Lee, S. U. Lee, M. H. Lee, *J. Am. Chem. Soc.* **2015**, *137*, 8018–8021.

[37] a) H. J. Bae, J. Chung, H. Kim, J. Park, K. M. Lee, T.-W. Koh, Y. S. Lee, S. Yoo, Y. Do, M. H. Lee, *Inorg. Chem.* **2014**, *53*, 128–138; b) T. Kim, J. Lee, S. U. Lee, M. H. Lee, *Organometallics* **2015**, *34*, 3455–3458.

[38] a) M. A. Baldo, M. E. Thompson, S. R. Forrest, *Nature* **2000**, *403*, 750–753; b) C. L. Lee, K. B. Lee, J. J. Kim, *Appl. Phys. Lett.* **2000**, *77*, 2280–2282.

[39] a) Y. You, S. Y. Park, *Dalton Trans.* **2009**, 1267–1282; b) W.-Y. Wong, C.-L. Ho, *Coord. Chem. Rev.* **2009**, *253*, 1709–1758; c) C. Fan, C. Yang, *Chem. Soc. Rev.* **2014**, *43*, 6439–6469.

[40] a) G.-X. Jin, *Coord. Chem. Rev.* **2004**, *248*, 587–602; b) S. Liu, Y.-F. Han, G.-X. Jin, *Chem. Soc. Rev.* **2007**, *36*, 1543–1560; c) X. Meng, F. Wang, G.-X. Jin, *Coord. Chem. Rev.* **2010**, *254*, 1260–1272; d) L. Jain, V. K. Jain, N. Kushwah, M. K. Pal, A. P. Wadawale, V. I. Bregadze, S. A. Glazun, *Coord. Chem. Rev.* **2014**, *258–259*, 72–118.

[41] a) K. Base, M. W. Grinstaff, *Inorg. Chem.* **1998**, *37*, 1432–1433; b) J. A. Weinstein, M. T. Tierney, E. S. Davies, K. Base, A. A. Robeiro, M. W. Grinstaff, *Inorg. Chem.* **2006**, *45*, 4544–4555; c) O. Crespo, M. C. Gimeno, A. Laguna, O. Lehtonen, I. Ospino, P. Pyykkö, M. D. Villacampa, *Chem. Eur. J.* **2014**, *20*, 3120–3127.

[42] J. Miao, H. Chen, M. Xu, B. Peng, Y. Nie, D. Sun, *Z. Naturforsch. B* **2011**, *66*, 65–68.

[43] Z.-J. Yao, G.-X. Jin, *Coord. Chem. Rev.* **2013**, *257*, 2522–2535.

[44] a) O. Crespo, M. C. Gimeno, P. G. Jones, A. Laguna, J. M. López-de-Luzuriaga, M. Monge, J. L. Pérez, M. A. Ramón, *Inorg. Chem.* **2003**, *42*, 2061–2068; b) O. Crespo, C. Díez-Gil, M. C. Gimeno, P. G. Jones, A. Laguna, I. Ospino, J. Tapias, M. D. Villacampa, R. Visbal, *Dalton Trans.* **2013**, *42*, 8298–8306.

[45] J. Dou, D. Zhang, Y. Zhu, D. Li, D. Wang, *Inorg. Chim. Acta* **2007**, *360*, 3387–3393.

[46] a) A. M. Prokhorov, P. A. Slepukhin, V. L. Rusinov, V. N. Kalinin, D. N. Kozhevnikov, *Chem. Commun.* **2011**, *47*, 7713–7715; b) A. M. Prokhorov, T. Hofbeck, R. Czerwieniec, A. F. Suleymanova, D. N. Kozhevnikov, H. Yersin, *J. Am. Chem. Soc.* **2014**, *136*, 9637–9642.

[47] J. R. Wright, T. J. Klingen, *J. Inorg. Nucl. Chem.* **1970**, *32*, 2853–2861.

[48] T. W. Bitner, T. J. Wedge, M. F. Hawthorne, J. I. Zink, *Inorg. Chem.* **2001**, *40*, 5428–5433.

[49] L. A. Leites, L. E. Vinogradova, V. N. Kalinin, L. I. Zakharkin, *Bull. Acad. Sci. USSR Div. Chem. Sci. (Engl. Transl.)* **1970**, *19*, 2437–2439 (Engl. Transl.).

[50] R. A. Harder, J. A. H. MacBride, G. P. Rivers, D. S. Yufit, A. E. Goeta, J. A. K. Howard, K. Wade, M. A. Fox, *Tetrahedron* **2014**, *70*, 5182–5189.

[51] E. S. Alekseyeva, A. S. Batsanov, L. A. Boyd, M. A. Fox, T. G. Hibbert, J. A. K. Howard, J. A. H. MacBride, A. Mackinnon, K. Wade, *Dalton Trans.* **2003**, 475–482.

[52] B. Peng, Y. Nie, J. Miao, Z. Zhang, M. Xu, G. Sun, *J. Mol. Struct.* **2012**, *1007*, 214–219.

[53] H. Kunkely, A. Vogler, *Inorg. Chim. Acta* **2004**, *357*, 4607–4609.

[54] M. J. Hardie, C. L. Raston, *CrystEngComm* **2001**, *3*, 162–164.

[55] R. L. Thomas, G. M. Rosair, A. J. Welch, *Acta Crystallogr., Sect. C* **1996**, *52*, 646–649.

[56] C. Tang, Z. Xie, *Angew. Chem. Int. Ed.* **2015**, *54*, 7662–7665; *Angew. Chem.* **2015**, *127*, 7772–7775.

[57] A. Laromaine, C. Viñas, R. Sillanpää, R. Kivekäs, *Acta Crystallogr., Sect. C* **2004**, *60*, o524–o526.

[58] R. Kivekas, F. Teixidor, C. Viñas, R. Nuñez, *Acta Crystallogr., Sect. C* **1995**, *51*, 1868–1870.

[59] C. Yang, private communication, CSD refcode XEBBEM02.

[60] H. Brunner, A. Apfelbacher, M. Zabel, *Eur. J. Inorg. Chem.* **2001**, 917–924.

[61] M. A. Fox, C. Nervi, A. Crivello, A. S. Batsanov, J. A. K. Howard, K. Wade, P. J. Low, *J. Solid State Electrochem.* **2009**, *13*, 1483–1495.

[62] M. V. Yarosh, T. V. Baranova, V. L. Shirokii, A. A. Erdman, N. A. Maier, *Russ. J. Electrochem.* **1993**, *29*, 789–790 (Engl. Transl.).

[63] M. V. Yarosh, T. V. Baranova, V. L. Shirokii, A. A. Erdman, N. A. Maier, *Russ. J. Electrochem.* **1994**, *30*, 366–368 (Engl. Transl.).

[64] F. Teixidor, J. Pedrajas, C. Viñas, *Inorg. Chem.* **1995**, *34*, 1726–1729.

[65] M. Borsari, M. Cannio, G. Gavioli, *Electroanalysis* **2003**, *15*, 1192–1197.

[66] G. F. Jin, J.-H. Hwang, J.-D. Lee, K.-R. Wee, I.-H. Suh, S. O. Kang, *Chem. Commun.* **2013**, *49*, 9398–9400.

[67] a) M. A. Fox, C. Nervi, A. Crivello, P. J. Low, *Chem. Commun.* **2007**, 2372–2374; b) K. Hosoi, S. Inagi, T. Kubo, T. Fuchigami, *Chem. Commun.* **2011**, *47*, 8632–8634; c) J. Kahlert, H.-G. Stammler, B. Neumann, R. A. Harder, L. Weber, M. A. Fox, *Angew. Chem. Int. Ed.* **2014**, *53*, 3702–3705; *Angew. Chem.* **2014**, *126*, 3776–3779.

[68] M. F. Hawthorne, T. D. Andrews, P. M. Garrett, F. P. Olsen, M. Reintjes, F. N. Tebbe, L. F. Warren Jr., P. A. Wegner, D. C. Young, *Inorg. Synth.* **1967**, *10*, 91–118.

[69] M. Tsuji, *J. Org. Chem.* **2003**, *68*, 9589–9597.

[70] M. F. Hawthorne, D. C. Young, P. M. Garrett, D. A. Owen, S. G. Schwerin, F. N. Tebbe, P. A. Wegner, *J. Am. Chem. Soc.* **1968**, *90*, 862–868.
[71] H. D. Smith Jr., C. O. Obenland, S. Papetti, *Inorg. Chem.* **1966**, *5*, 1013–1015.
[72] L. I. Zakharkin, M. N. Zhubeova, A. V. Kazantsev, *J. Gen. Chem. USSR* **1972**, *42*, 1013–1017 (Engl. Transl.).
[73] R. P. Alexander, H. Schroeder, *Inorg. Chem.* **1963**, *2*, 1107–1110.
[74] R. Coult, M. A. Fox, W. R. Gill, P. L. Herbertson, J. A. H. MacBride, K. Wade, *J. Organomet. Chem.* **1993**, *462*, 19–29.
[75] M. M. Fein, J. Bobinski, N. Mayes, N. Schwartz, M. S. Cohen, *Inorg. Chem.* **1963**, *2*, 1111–1115.
[76] J. C. de Mello, *Adv. Mater.* **1997**, *9*, 230–232.
[77] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122.
[78] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339–341.

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